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Surface-Enhanced Raman Spectroscopy of Electrochemically

Characterized Interfaces. Transition-Metal Isothiocyanate

Adsorbates at Silver Adsorbates

by

M. A. Tadayyoni, Stuart Farquharson, Tomi T-T. Li

and Michael J. Weaver

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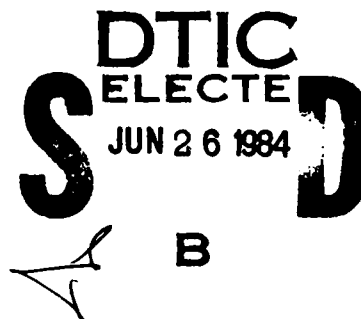
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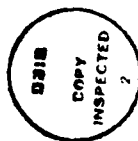**DTIC**

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Surface-enhanced Raman (SER) spectra have been obtained at the silver-aqueous interface for nine Cr^{III}, Co^{III}, Ru^{II}, and Rh^{III} ammine or ethylenediamine complexes containing one or more thiocyanates as surface bridging groups. These complexes provide stereochemically well-defined adsorbates having at least one sulfur surface binding site but with electronic properties that differ substantially from thiocyanate itself. The dependence of the SER spectra were examined in each case over a potential range where the complexes are stable with respect to reduction or oxidation, and where the adsorbate

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coverage remained close to a monolayer. The adsorbate coverage could be evaluated in several cases from the faradaic charge required for one-electron reduction. SER spectra were obtained using a spectrograph-optical multi-channel analyzer (OMA) as well as a conventional scanning spectrometer. This enabled the rapid reversible component of the SERS potential dependence to be separated from the irreversible signal decay associated with surface rearrangement. SERS bands due to metal ammine and internal ammine vibrations were observed in addition to those associated with internal thiocyanate and ligand-surface vibrations. The intensities and frequencies of most of these SERS bands were only mildly dependent upon the electrode potential. However, the peak frequency and bandshape of the thiocyanate C-N stretching mode (ν_{CN}) was found to be sensitive both to the electrode potential and the nature of the coordinated transition metal. These differences can be understood in terms of electron withdrawal by the silver surface.

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SURFACE-ENHANCED RAMAN SPECTROSCOPY OF

ELECTROCHEMICALLY CHARACTERIZED INTERFACES.

TRANSITION-METAL ISOTHIOCYANATE ADSORBATES AT SILVER ~~ELECTRODES~~ *ADSORBATES*

M. A. Tadayyoni, Stuart Farquharson, Tomi T-T. Li
and Michael J. Weaver*

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907, U.S.A.

Abstract

Surface-enhanced Raman (SER) spectra have been obtained at the silver-aqueous interface for nine Cr^{III}, Co^{III}, Ru^{II}, and Rh^{III} ammine or ethylenediamine complexes containing one or more thiocyanates as surface bridging groups. These complexes provide stereochemically well-defined adsorbates having at least one sulfur surface binding site but with electronic properties that differ substantially from thiocyanate itself. The dependence of the SER spectra were examined in each case over a potential range where the complexes are stable with respect to reduction or oxidation, and where the adsorbate coverage remained close to a monolayer. The adsorbate coverage could be evaluated in several cases from the faradaic charge required for one-electron reduction. SER spectra were obtained using a spectrograph-optical multichannel analyzer (OMA) as well as a conventional scanning spectrometer. This enabled the rapid reversible component of the SERS potential dependence to be separated from the irreversible signal decay associated with surface rearrangement. SERS bands due to metal ammine and internal ammine vibrations were observed in addition to those associated with internal thiocyanate and ligand-surface vibrations. The intensities and frequencies of most of these SERS bands were only mildly dependent upon the electrode potential. However, the peak frequency and bandshape of the thiocyanate C-N stretching mode (ν_{CN}) was found to be sensitive both to the electrode potential and the nature of the coordinated transition metal. These differences can be understood in terms of electron withdrawal by the silver surface.

We have recently been examining surface-enhanced Raman scattering (SERS) for a variety of adsorbates at the silver-aqueous interface for which quantitative information on the surface concentration can be obtained by electrochemical means.[1-6] These adsorbates include those that engage in reversible one-electron transfer reactions within the available potential range at silver electrodes. This enables quantitative assessments to be made of the response of the SERS signals to variations in the surface concentration of the Raman scatterer brought about by alterations in redox[5] as well as adsorption-desorption equilibria.[1-4] Another virtue of employing electroactive adsorbates is that their surface concentrations can often be readily obtained by using faradaic perturbation techniques. Although we have found that chronocoulometry often yields unreliable adsorption data at solid electrodes,[7] rapid scan cyclic voltammetry has proved to be a valuable means of obtaining such data at silver surfaces.[5b,7,8] For electroinactive adsorbates at silver, accurate surface concentration data can be obtained in favorable cases from measurements of the differential double-layer capacitance as a function of electrode potential and bulk adsorbate concentration in constant ionic strength media.[2,9]

These results demonstrate that there are approximate correlations between the SERS intensity and the potential-dependent adsorbate coverage, at least when the SERS data are gathered sufficiently rapidly to avoid the irreversible signal decay associated with loss of Raman-active sites.[1,4] An interesting exception is adsorbed thiocyanate in that substantial decreases in intensity of the SERS modes occur as the electrode potential is made more negative, even under conditions where the coverage of this adsorbate remains

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close to a monolayer. We have suggested that these intensity decreases
are most likely due to field-induced structural changes, such as reorientation,
in the adsorbate layer.[1,2,4]

More recently, we have been examining SERS of a number of transition-
metal N-bound thiocyanate complexes ("isothiocyanates"). These have the
general formula $M^{III}(NH_3)_{6-x}(NCS)_x$ or $M^{III}(en)_2(NCS)_2$, where en = ethylene-
diamine and $M^{III} = Cr^{III}$, Ru^{III}, Co^{III}, Os^{III}, or Rh^{III}. These adsorbates
were selected for detailed study for several reasons. Firstly, in contrast
to uncoordinated thiocyanate the complexes can only bind to the surface
via the sulfur atom since the nitrogen is rigidly bound to the transition-
metal cation. They are also stable with respect to photochemical dissociation
by the 647 nm light used for Raman excitation. Such substitution inert
complexes therefore offer important advantages over labile complexes such as
cadmium thiocyanates that have also been studied recently using SERS.[10]
Secondly, they provide a means of exploring the influence of alterations
in the electronic structure upon the vibrational modes brought about by
variations in the transition-metal cation. Such electronic factors have
previously been suggested to influence adsorbate-surface binding involving
thiocyanate and related bridging ligands.[11] Thirdly, such adsorbates,
especially those containing two or more thiocyanates in the cis-configuration,
provide unusually rigid and stereochemically well-defined adsorbates.[12]
They exhibit a number of clearly identifiable vibrational modes associated
with the nonbridging ammine as well as the bridging thiocyanate ligands.

In addition, we have recently examined the electroreduction kinetics of adsorbed Cr(III) and Co(III) complexes bound to silver, platinum, and gold surfaces via thiocyanate, azide, and halide bridging ligands.[7,8,13] These complexes provide valuable model adsorbates with which to examine the fundamental influences of the adsorbate-surface interactions upon electrochemical reactivity. The evaluation of the vibrational properties of such electroactive adsorbates and the comparison with corresponding data for the bulk-phase complexes is therefore of considerable interest.

Surface-enhanced Raman (SER) spectra obtained for these thiocyanate-bridged adsorbates at the silver-aqueous interface are reported here, along with corresponding data for these and related systems as bulk solids obtained using normal Raman (NR) and infrared (IR) spectroscopy. Taken together, the results shed light both on the nature of the adsorbate-surface interactions and some of the major factors that influence SERS in these and related systems.

Experimental

The various thiocyanate complexes were prepared as solid perchlorate, hexafluorophosphate, or chloride salts using literature procedures as follows: $Cr(NH_3)_5NCS^{2+}$[14], $c-Cr(NH_3)_4(NCS)_2^+$[15], $c-Cr(en)_2(NCS)_2^+$[16], $t-Cr(en)_2(NCS)_2^+$,[17] $c-Co(en)_2(NCS)_2^+$,[18] $Ru(NH_3)_5NCS^{2+}$,[19] $Rh(NH_3)_5NCS^{2+}$.[20] $t-Cr^{III}(NH_3)_2(NCS)_4 \cdot Ag^I$ was prepared from $K \cdot Cr(NH_3)_2(NCS)_4$ (Alfa Chemicals) by precipitation with $AgNO_3$ (cf. ref. 21). $K_3 \cdot Cr(NCS)_6$ (Alfa Chemicals) was recrystallized before use. Ammine or ethylenediamine deuteration of these complexes in solution was achieved by dissolving them in a small volume of neutral D_2O, and acidifying before dilution with water.[24] The potassium chloride and sodium perchlorate used as supporting electrolytes

were reagent grade, and were recrystallized prior to use. Water was purified by means of a "Milli Q" system (Millipore Inc.).

Both electrochemical and SERS measurements utilized a silver electrode of rotating disk construction having a disk radius of 0.2 cm surrounded by a teflon sheath. The electrode was mechanically polished on a wheel successively with 5, 1, and 0.3 μm alumina immediately prior to immersion in the solution. The cell used for SERS measurements was of conventional electrochemical design, being constructed of glass and having a working compartment (ca 10 mL volume) containing the silver and platinum counter electrodes separated from another compartment containing a saturated calomel electrode (s.c.e.) by means of a fine glass frit. The bottom of the working compartment consisted of a 1/16" thick glass flat through which the laser beam was illuminated vertically onto the silver electrode surface. The cell was tilted at a suitable angle so that the scattered light could be collected at 90° to the incident beam and about 60° to the electrode surface.

The Raman spectra were gathered using either a conventional scanning spectrometer or using a spectrograph-optical multichannel analyzer (OMA) arrangement. The former consisted of a SPEX 1403 double monochromator equipped with holographic gratings (1800 gr/mm), a RCA C31034 photomultiplier tube, a SPEX DPC-2 photon counter, a SPEX CD2 Compudrive and a Kipp and Zonen BD40 strip chart recorder. The Raman scattered light was focussed into the entrance slit using a Olympus F1-2 55 mm focal length camera lens. The latter arrangement consisted of a SPEX 1877 triple spectrograph with a 600 gr/mm grating in the filter stage and either 1200 or 1800 gr/mm in the dispersion stage, a PAR 1420-3 photodiode array detector, a PAR 1218 detector controller, and a PAR 1215 control console.

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The Raman scattered light was collected by means of a SPEX 1459 illuminator. Laser irradiation was either a Spectra-Physics 165 Kr^+ laser operated at 647.1 nm or Ar^+ laser at 514.5 nm. The laser beam was spot focussed on the electrode surface, typically using 100-200 mW power at the sample. The scanning spectrometer system was primarily employed for initial studies or for detailed measurements where the SERS signals were stable over the time period (ca 20-60 mins) necessary when making a series of measurements using this approach. This system could also be utilized for Raman frequencies down to ca 100 cm^{-1}, whereas stray light from the spectrograph effectively limited the OMA system to recording frequencies above ca 200 cm^{-1}. However, the OMA was preferred for most measurements where extensive potential-dependent data were obtained since good-quality spectra could be obtained in only 1-2 secs. The OMA also enabled SER spectra to be obtained for a number of these complexes using 514.5 nm as well as 647.1 nm light, even though relatively rapid photolysis commonly occurs at the former wavelength.[22]

The silver electrode was mildly roughened in order to optimize the SER signal intensity by means of one to five oxidation-reduction cycles (ORC). This generally entailed stepping the potential from ca -150 mV to +350 mV versus s.c.e., returning after the accumulation of ca 20-40 mC cm^{-2} anodic charge. Stronger SER signals for the thiocyanate complexes were generally obtained in the absence of laser irradiation during the ORC (contrast the behavior of thiocyanate in ref. 23); this procedure was therefore usually follwed. The ORC's were performed either in a separate 0.1 $\underline{M}$ KCl solution and rapidly transferred to the solution of interest, or directly in the latter if this contained chloride ions, with essentially identical results. Normal Raman spectra of the bulk-phase solid complexes were obtained with 647.1 nm irradiation,

mostly using solid pellets mounted on the tip of a spinning rod to minimize photodecomposition. The bulk-phase Raman spectra utilized to estimate surface enhancement factors (vide infra) were obtained either in a Nujol mull or in dimethylsulfoxide solution. Infrared spectra were obtained from 600-3000 cm^{-1} on a Perkin-Elmer Model 267 spectrometer using KBr pellets or Nujol mulls, and from 50-500 cm^{-1} on a Digilab FTS 20 spectrometer using polyethylene disks.

Potential control during the electrochemical SERS measurements was achieved using a PAR 173/179 potentiostat. Rapid linear sweep voltammetry additionally employed a PAR 175 potential programmer, the voltammograms being recorded with a Nicolet 2090-1 digital oscilloscope coupled with a Houston 2000 X-Y recorder. Differential capacitance measurements were made using a phase-sensitive detection method.[9] This utilized a PAR 173/179 potentiostat and a PAR 5204 lock-in amplifier with internal oscillator, interfaced to an LSI 11-23 microcomputer in order to provide a direct readout of both the capacitance and resistive components of the cell impedance.

All solutions were degassed with nitrogen or argon prior to the electrochemical measurements. All electrode potentials are quoted versus the s.c.e., and all measurements were made at room temperature, 23 + 1°C.

Results

Table I contains a summary of peak frequencies for the various thiocyanate vibrational modes for each complex bound to the silver electrode at four electrode potentials. For comparison, it also contains corresponding data for the bulk-phase complexes. The SERS data were generally obtained using 1-2 mM of the thiocyanate complex in either 0.01 or 0.1 M HCl, or 0.1 M NaClO$_4$, acidified in each case with 2 mM HClO$_4$ to avoid any base-catalyzed hydrolysis. As for adsorbed thiocyanate[1] all three internal thiocyanate modes, the C-N

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stretch (ν_{CN}, ca 2100 cm^{-1}), and C-S stretch (ν_{CS}, ca 730-800 cm^{-1}), and the N-C-S bend (δ_{NCS}, ca 450 cm^{-1}), were observed for most complexes, although the ν_{CS} band was very weak. These assignments were made by means of their characteristic frequencies (vide infra). In addition, a band around 210-220 cm^{-1} appeared for most complexes (Table I), attributed to a surface-sulfur stretching mode (ν_{Ag-S}) by comparison with SERS for adsorbed thiocyanate.[1]

The least negative potential in Table I, -150 mV, was chosen since it is significantly negative of the potential, ca 0 mV, where anodic oxi   ɔn of the silver surface commences in these media. However, some reduc of c-Co(en)$_2$(NCS)$_2^+$ occurs even at -150 mV. Indeed, spectra obtaine this adsorbate at more negative potentials are indistinguishable from those for free thiocyanate. This is expected since these ligands are released upon the one-electron reduction of Co(III). The Cr(III) thiocyanate adsorbates can be examined over a wider potential range; although their one-electron electroreductions are also chemically irreversible they do not occur at a significant rate until around -600 mV[7,8] (vide infra). The SERS of Rh(NH$_3$)$_5$NCS^{2+} was also examined since Rh(III) reduction does not commence until ca -800 mV. Unfortunately, the spectra for this adsorbate were sufficiently weak that the ν_{CN} mode appeared at only the most positive potentials. However, uniformly intense SER spectra were obtained for Ru(NH$_3$)$_5$NCS^{2+} from -150 to -900 mV. Although this complex is reduced at -140 mV,[25] the resulting Ru(II) species, Ru(NH$_3$)$_5$NCS$^+$, is also substitutionally inert and does not undergo further reduction within this potential range.

Representative SER spectra for a typical complex, c-Cr(NH$_3$)$_4$(NCS)$_2^+$, in the frequency regions 160-500 cm^{-1} and 2050-2200 cm^{-1} are shown as a function of potential in Fig. 1, along with bulk-phase Raman spectrum. Besides the bridging thiocyanate modes already noted, several other bands appear in the frequency region 200-500 cm^{-1} for this and the other thiocyanate-bound adsorbates. The band around 460 cm^{-1}, ascribed in part to δ_{NCS}, also

appears to be due to a metal-ammine stretching mode ν_{M-NH_3}. This accidental degeneracy can be removed by deuterating the ammine ligand, whereupon the ν_{M-ND_3} mode shifted to about 420 cm^{-1}, (shown as a dashed curve in Figures 1A and D). This frequency decrease is consistent with that expected (35 cm^{-1}) on the basis of the greater mass of the ND_3 versus the NH_3 ligand. In addition, bands around 240, 270, and 330 cm^{-1} were often obtained for this and most other complexes. Since the 240 cm^{-1} band only appeared in the presence of chloride and occurs at the same frequency as in pure chloride electrolytes,[26] it is assigned to a surface-chloride stretching mode. This band was often obscured by the surface-sulfur stretch at 210-220 cm^{-1}.

The other two bands are less straightforward to assign. Barely discernable peaks were seen around these frequencies in the bulk-phase Raman spectra (eg. Fig. 1A). However, much stronger bands were seen in the IR spectra for the Cr(III) thiocyanato ammine complexes. (For example, these bands occurred at 260 and 325 cm^{-1} in the IR spectra of $c\text{-}Cr(NH_3)_4(NCS)_2^+$). Since only a band at 270 cm^{-1} was seen in the IR spectrum of $Cr(NH_3)_6^{3+}$, we tentatively attribute the corresponding SERS band to the asymmetric NMN bending mode, δ_{NMN}, on the basis of the assignments detailed in ref. 27. This mode is expected to shift to significantly (ca 10-20 cm^{-1}) smaller frequencies upon ammine deuteration;[27] although some shift was indeed observed in the SER spectra under these conditions, the band was insufficiently well defined to enable a quantitative conclusion to be made on this point. Attempts were made to detect internal ammine stretching and bending modes; for example ν_{NH} bands should occur around 3200 cm^{-1}.[27] However, these were apparently too weak to be observed in the SER spectra.

For the ethylenediamine complexes, a number of other bands were observed in both the SER and bulk-phase Raman spectra which are clearly due to internal

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ethylenediamine modes. A prominent band at 485 cm^{-1} was generally observed, somewhat (2-3 fold) more intense than ν_{M-NH_3} for the ammine complexes. This is assigned to a metal-ethylenediamine stretching mode, ν_{M-en}; as expected this shifted to about 460 cm^{-1} upon ethylenediamine deuteration. Several other bands were seen in the range 500-2000 cm^{-1} which can be identified as arising from internal ethylenediamine modes by comparison with NR and IR spectra for these and related ethylenediamine complexes.[28] For example, peaks were seen for t-$Cr(en)_2(NCS)_2^+$ at 800, 880, 1050, 1285, 1400, 1595, and 1895 cm^{-1}.

The SERS metal-ammine, metal-ethylenediamine, and internal ethylenediamine bands are relatively narrow (full width at half maximum, FWHM $\approx$ 15-25 cm^{-1}), similarly to that seen in the bulk-phase Raman and IR spectra. However, the SERS ν_{CN} bands (FWHM ~ 40-65 cm^{-1}) are markedly broader than those in the NR and IR bands (FWHM ~ 20-30 cm^{-1}) and significantly dependent upon the nature of the transition-metal cation. This is exemplified by Fig. 2, which contains SERS ν_{CN} bands for NCS^-, $Cr(NH_3)_5NCS^{2+}$, and $Ru(NH_3)_5NCS^{2+}$ at -300 mV plotted on a common frequency axis with the peak intensities normalized to a single value. The ν_{Ag-S} bands were also typically broad, FWHM ~ 30-40 cm^{-1} (Fig. 1).

Particular attention was paid to the dependence of the SERS band intensities and peak frequencies upon the electrode potential. Whenever convenient the OMA system was used for these measurements in order to minimize the time dependence of the Raman intensities associated with the irreversible loss of Raman-active sites.[1,4] This procedure enables the rapid "reversible" portion of the potential dependence to be determined separately from the irreversible component.[1,4] We have noted previously that the intensity of

ν_{CN} and ν_{Ag-S} for adsorbed NCS^- decreases markedly as the potential is made more negative. In contrast, the peak intensity and bandshape (and hence the integrated band intensity) for all four Cr(III) thiocyanate complexes (Table I) remained approximately constant (within ca 20-30%) between -150 and ca -550 mV, although the intensity typically increased by 20-30% between -150 and -300 mV. By comparison, the reversible intensity of the SERS ν_{CN} mode for NCS^- decreases by ca 2-3 fold from -150 to -600 mV.[1]

Essentially the same results were obtained for the ν_{CN}, ν_{M-NH_3}, and ν_{Ag-S} modes by using the scanning spectrometer system, although marked intensity decreases were seen around -500 to -600 mV. These were traced to an increasingly rapid temporal decay of the SERS signals as the potential is made more negative in this region. Such potential dependence could be largely eliminated by gathering potential-dependent data within 10 sec or so using the OMA. Altering the potential more negative of ca -600 mV yielded a rapid and almost complete loss of the ν_{CN} band. This is undoubtedly due to irreversible reduction of the Cr(III) adsorbates since the voltammetric reduction waves occur in this potential region.[8,29]

The potential-dependent SERS of $Ru(NH_3)_5NCS^{2+}$ is of particular interest in this regard; as noted above the Ru(III)/(II) couple is chemically reversible so that the Ru(II) product should stay intact at the electrode surface over an especially large potential range. Indeed, the intensity and bandshape of the ν_{CN} mode for this adsorbate remains virtually constant (±10%) throughout the potential region -150 to -900 mV. The ν_{M-NH_3} mode at

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455 cm^{-1} behaved similarly, although the ν_{Ag-S} mode was too weak to enable
its reversible intensity-potential dependence to be determined. The
frequency of ν_{M-NH_3}, 450 cm^{-1}, was also essentially independent of potential
in the region -50 to -750 mV. This value is consistent with the presence
of Ru(II) rather than Ru(III); we therefore designate this adsorbate as
$Ru(NH_3)_5NCS^+$ rather than $Ru(NH_3)_5NCS^{2+}$. The peak frequency of the ν_{CN} mode
for adsorbed $Ru(NH_3)_5NCS^+$ decreased progressively with increasing negative
potential (Fig. 3); this potential dependence was smaller than those seen
for the Cr(III) adsorbates (Table I).

That these complexes are adsorbed in amounts close to a monolayer under
the conditions employed for the SERS measurements were deduced from three lines
of evidence. Firstly, the Cr(III) complexes and $c-Co(en)_2(NCS)_2^+$ can be
reduced by an irreversible one-electron transfer at potentials prior to the
negative limit of silver in mildly acidic media (ca -800 to -900
mV). By employing linear sweep voltammetry with small bulk reactant
concentrations ($\leq$ 0.1 m$\underline{M}$) and rapid sweep rates ($\geq$ 10 V sec^{-1}) the initially
adsorbed species provides the major contribution to the faradaic reduction
wave, enabling the extent of adsorption at the initial potential to be
obtained.[7,8] Details of the experimental results at polished silver electrodes
are given in refs. 7 and 8. Surface reactant concentrations close to that
expected for a monolayer (1.5 to 2 x 10^{-11} mol cm^{-2}) were typically
obtained. No electroactivity could be detected for adsorbed $Ru(NH_3)_5NCS^+$ or
$Rh(NH_3)_5NCS^{2+}$ at silver from -100 to -800 mV. Similar results were obtained
at electrochemically roughened silver, the extent of adsorption (in moles per
apparent cm^{-2}) simply being increased in proportion to the roughness factor
RF (ratio of actual to apparent area) as determined by the corresponding
increase in the background capacitance.[2] (Values of RF around 1.5-2.5
were typically found by using the above ORC roughening procedure.[2])

A second line of evidence indicating monolayer adsorption was obtained from differential capacitance-potential (C_d-E) data. Addition of ca 0.1 m$\underline{M}$ or more of the thiocyanate complex to 0.1 $\underline{M}$ KCl yielded marked decreases in the capacitance in the potential region -50 to -500 mV, indicating that the complex was replacing the initially adsorbed chloride ions[2] (cf Fig. 1 of ref. 1). Thirdly, the electroreduction kinetics of the Cr(III) complexes display apparent electrochemical reaction orders substantially below unity; this is again indicative of adsorbate coverages approaching saturation at the reactant concentrations (0.5 - 2 m$\underline{M}$) employed.[8]

Some measurements of the SERS ν_{CN} region were made using 514.5 nm as well as 647.1 nm laser excitation. Although relatively rapid photo-decomposition occurred, especially for the Cr(III) complexes,[22] a satisfactory set of potential-dependent data could be obtained without significant signal decay using the OMA. Essentially similar SERS results were obtained using 514.5 and 647.1 nm irradiation. However, the ν_{CN} bandshapes were slightly different, 5-10 cm^{-1} higher frequencies being typically obtained with the former laser line. This result was obtained irrespective of laser illumination conditions during the ORC.

The intensities of the thiocyanate SERS modes for the various complexes (excepting $Rh(NH_3)_5NCS^{2+}$) are closely similar to one another as well to those for free thiocyanate at the least negative potentials (-100 to -200 mV). Similar results were obtained for the ν_{CN} band using 541.5 nm as well as 647.1 nm irradiation. We have made extensive comparisons of the integrated SERS and bulk-phase Raman intensities for these and a variety of other adsorbates. These measurements when coupled with the surface concentration

data enable estimates of the "surface enhancement factor", SEF, (i.e. the increase in Raman scattering intensity per molecular upon adsorption) to be obtained. Details are given elsewhere.[31] Broadly speaking, the SEF values for the thiocyanate adsorbates are insensitive to their electronic structure and indeed are similar (within 2-5 fold) to those for related inorganic adsorbates. Representative values of SEF for the ν_{CN} mode of NCS^-, $Cr(NCS)_6^{3-}$, and $Cr(NH_3)_5NCS^{2+}$ are at -300 mV; 2.5×10^6, 3.5×10^6, and 6×10^6, respectively (cf SEF for pyridine[33]). An examination was also made of the relative SEF values for the ν_{CN} and ν_{M-N} bands for adsorbed $Cr(NH_3)_5NCS^{2+}$ and $c-Cr(NH_3)_4(NCS)_2^+$. Although somewhat dependent upon the experimental conditions, the SEF values for the ν_{CN} bands tend to be ca 2-5 fold larger than the corresponding ν_{M-N} bands.

Discussion

The marked (≥ 30 cm^{-1}) increases in ν_{CN} upon adsorption of the various thiocyanate complexes (Table I) are similar to that seen when binding the

sulfur atom of metal isothiocyanate complexes to another metal cation.[34] Similar frequency shifts also occur for binding NCS$^-$ to a silver electrode (Table I)[1] and to metal cations via the sulfur atoms.[34] These shifts can be understood in part through an increase of the C-N force constant via withdrawal of electron density from the sulfur.[34] This result for NCS$^-$ provides strong evidence that adsorption at silver involves the sulfur rather than the nitrogen atom.[1,10] The similar behavior seen for the present thiocyanate complexes supports this conclusion since the sulfur atom clearly provides the only means of surface binding. The significantly (10-30 cm^{-1}) higher values of ν_{CN} for the adsorbed complexes versus that for adsorbed NCS$^-$ at the same electrode potential (Table I) recalls the especially high values of ν_{CN} seen for a number of metal complexes where thiocyanate is acting as a bridge between a pair of metal ions.[34] Comparison of the corresponding values of ν_{CN} for each complex with that for NCS$^-$ shows that comparable increases (10-40 cm^{-1}) in ν_{CN} are brought about by nitrogen coordination of NCS$^-$ to Cr(III), Co(III), Ru(II), and Rh(III) in both bulk-phase and adsorbed environments (Table I). This suggests that the perturbation of the C-N bond due to sulfur surface coordination is roughly additive with that resulting from transition metal-nitrogen binding. However, it is interesting to note that the increase in ν_{CN} associated with the latter tends to be largest for the low-spin d^6 metals Co(III) and Rh(III); these metals are expected to yield the largest increase in the C-N force constant via metal-thiocyanate π bonding.[11]

The frequency of the ν_{CS} band for adsorbed Cr(NH$_3$)$_5$NCS^{2+} (790 cm^{-1}) is also similar to that seen for several bridging thiocyanate complexes,[34] and noticeably larger than for adsorbed thiocyanate (735 cm^{-1}, Table I) as

well as in other terminal S-bound environments.[34] The latter frequency shift is consistent with vibrational coupling with the metal-nitrogen bond.[34]

The comparison between ν_{CN} for the complexes when bound to the silver surface and when bound to bulk-phase Ag(I) is anticipated to provide valuable insight into the nature of surface bonding for these systems. Comparison of the relevant data in Table I shows that the values of ν_{CN} for the adsorbed Cr(III) complexes at the most positive potential, -150 mV, approach that for the binuclear complex $t-Cr^{III}(NH_3)_2(NCS)_4Ag^I$ (2140 cm^{-1}). The potential region in Table I is considerably positive of the potential of zero charge (p.z.c.), so that the silver surface carries a large positive electronic charge density.[1] However, the average "formal oxidation state", x, of the surface silver atoms under these conditions is considerably less than unity.[1] For example, $x \approx 0.2$ for a monolayer of NCS$^-$ anions at -150 mV, the p.z.c. (i.e. where x = 0) being around -1800 mV under these conditions.[1,35] Such estimations of x are precluded for the metal thiocyanate complexes since the required differential capacitance data cannot be obtained over a sufficiently wide potential range. However, similar results are expected on the basis of the demonstrated similarities in the adsorption thermodynamics of thiocyanate and Cr(III) thiocyanates at mercury electrodes.[12]

We have previously pointed out that the potential dependence of ν_{CN} and ν_{Ag-S} for adsorbed thiocyanate is rather larger than might be expected on the basis of changes in bond polarization effects alone.[1] It was noted that this might arise in part from the reorientation and/or adsorption site redistributions that apparently yield the corresponding changes in intensity and FWHM of these bands. The noticeably smaller reversible potential dependence

of ν_{CN} for adsorbed $Ru(NH_3)_5NCS^+$ (18 cm^{-1} V^{-1}, Fig. 3) than for NCS^- (up to 40 cm^{-1} V^{-1})[1] is particularly pertinent. Given that the intensity and bandshape of the former is essentially independent of potential, this smaller potential dependence of ν_{CN} might then be taken as the "true" value associated with bond polarization effects alone. However, x is only mildly dependent upon the electrode potential E (roughly dx/dE $\sim$ 0.1 V^{-1}).[1] The perturbations in ν_{CN} induced by surface binding are therefore more pronounced than would be expected on the basis of the effective ionic charge of the surface silver atoms.[1]

Nevertheless, an array of charged metal surface atoms might be anticipated to have distinctly different bonding properties to those of an isolated metal ion. In addition, it is likely that the surface sites primarily responsible for SERS of these and related adsorbates are associated with adatoms or, more likely, metal clusters.[1] These sites are expected to have distinctly different electronic and stereochemical properties to those of a plane array of surface atoms.[36] In particular, the electronic charge of such sites should be significantly more positive than the plane lattice sites. Consequently SERS may arise from surface sites that are more electron deficient (i.e. have larger x) than for the "ensemble average" as monitored by the differential capacitance. Such metal clusters would also be expected to provide a variety of subtly different coordination environments since their electronic properties will be sensitive to their size and structure. This provides an explanation for the unusual breadth and asymmetry of the SERS ν_{CN} and ν_{Ag-S} bands in relation to the nonbridging ν_{M-NH_3} modes (Figs. 1, 2) since the former should be much more sensitive to the coordination environment of the adsorbed sulfur atom.

The observed insensitivity of the thiocyanate SERS intensities to the nature of, or even the presence, of a transition metal coordinated to the

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thiocyanate nitrogen suggests that the electronic structure of the adsorbate exerts little influence upon SERS of these systems. The similar SERS intensities and SEF values seen for the ν_{CN} band for the metal complexes and free thiocyanate using 514.5 nm irradiation is especially interesting in that this wavelength is situated amidst a relatively intense d-d adsorption band for most of the transition-metal adsorbates.[22] This band is absent for free thiocyanate and silver thiocyanate. This suggests that a "resonance Raman" effect associated with electronic excitation within the adsorbate is not providing a major contribution to SERS for these systems.[31]

It remains to consider the possible dependence of the surface Raman intensities upon the electrode potential. Given that the coverage of adsorbed thiocyanate remains close to a monolayer, at least in the potential range −100 to −600 mV, the observation that the intensity of the ν_{CN} and ν_{Ag-S} bands decreases sharply with increasing negative potential in this region indicates that the surface enhancement factor (SEF) is also diminished in roughly the same proportion.[1] This result has been interpreted as indicating that the polarizability of the SERS-active adsorbate is a strong function of the electrode potential, associated with a mechanism arising from surface optical resonance.[37] However, as noted above the potential-induced decreases in SEF may well arise at least partly from a change in adsorbate orientation.[1,2,4] The latter is supported by the "peaked" structure of the differential capacitance-potential (C_d-E) curves for adsorbed thiocyanate within this potential region, signaling potential-inded changes in the dielectric properties of the adsorbed thiocyanate layer.[2] Interestingly, capacitance data

gathered for adsorbed monolayers of $Cr(NH_3)_5NCS^{2+}$ and $c\text{-}Cr(NH_3)_4(NCS)_2^{+}$ in the potential region -100 to -600 mV prior to their electroreduction yield relatively flat featureless $C_d\text{-}E$ curves similar to those found for bromide or iodide monolayers.[38] This suggests that the transition-metal thiocyanate adsorbates do not undergo any noticeable structural alterations within this potential region. The roughly potential-independent SEF observed for these adsorbates, particularly $Ru(NH_3)_5NCS^{+}$, under these conditions is in harmony with this finding, and suggests that the potential dependence of SEF for thiocyanate arises primarily from changes in adsorbate structure rather than in the effective polarizability.

Conclusions

We believe that the foregoing provides a demonstration of the considerable virtues of employing structurally simple transition-metal complexes as model adsorbates for exploring the SERS effect in electrochemical environments. The use of substitution-inert complexes containing one or more strongly adsorbing ligands enable systematic changes to be made in the electronic and stereochemical properties of the adsorbate while the nature of the surface binding remains unchanged. While the SERS frequencies are noticeably dependent upon the electrode potential as well as the electronic structure of the coordinated transition metal, the SERS intensities are relatively insensitive to these factors. Vibrational bands associated with nonbridging as well as bridging ligand modes appear in the SER spectra, albeit with diminished intensity.

It is hoped that these results will spawn further efforts to apply
SERS to structurally well-defined adsorbates at interfaces that can be
characterized independently by electrochemical means. Unfortunately, much
of the recent experimental work focussing on the elucidation of the surface
enhancement mechanisms has employed electrochemical interfaces of unknown
surface composition and structure so that the conclusions are often of
questionable validity. However, the judicious selection of structurally well-
defined adsorbates along with the utilization of surface electroanalytical
techniques should aid such mechanism diagnoses, and perhaps more importantly,
lay the groundwork for further applications of SERS to surface electrochemistry.

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Table I. Vibrational frequencies (cm^{-1}) for thiocyanate modes in transition-metal ammine and ethylenediamine complexes at silver electrodes and in bulk-phase environments.

| Complex | Mode[a] | Silver Electrode, mV vs. s.c.e.[b] | | | | Bulk Phase | |
		−150	−300	−450	−600	Uncord.[c]	Ag(I)[f]
NCS⁻	ν_{Ag-S}	215	210	205			
	δ_{NCS}	450	450	450			
	ν_{CS}	735	735	735		750	720
	ν_{CN}	2115	2110	2102	2095	2055	2140[e]
Cr(NH$_3$)$_5$NCS^{2+}	ν_{Ag-S}	220	220	215			
	δ_{NCS}	460	460	460		460	
	ν_{CS}	790	790	790		960	
	ν_{CN}	2135	2130	2125	2118	2090(sh) 2080	
c-Cr(NH$_3$)$_4$(NCS)$_2^+$	ν_{Ag-S}	225	225	215			
	δ_{NCS}	460	460	455		460	
	ν_{CN}	2165 2130	2155 2125	2120	2114	2100(sh) 2082[e]	
t-Cr(NH$_3$)$_2$(NCS)$_4^-$	ν_{Ag-S}	215	210				~200[g]
	δ_{NCS}	460	460			450	450
	ν_{CN}	2150(sh) 2120	2150(sh) 2120			2110 2060	2140 2120
c-Cr(en)$_2$(NCS)$_2^+$	ν_{Ag-S}	232	225	215			
	δ_{NCS}	460	460	460		460	
	ν_{CN}	2125	2119	2114	2107	2098[e] 2080	
t-Cr(en)$_2$(NCS)$_2^+$	ν_{Ag-S}	207	205				
	δ_{NCS}	460	460	460		465	
	ν_{CN}	2125	2119	2113	2108	2100 2085	
Cr(NCS)$_6^{3-}$	ν_{Ag-S}	205	205				
	δ_{NCS}	460	460			475	465
	ν_{CN}	2140	2140			2090	2150 2120(sh)

Complex	Mode[a]	-150	-300	-450	-600	Uncord.[c]	Ag(I)[f]
c-Co(en)$_2$(NCS)$_2^+$	ν_{Ag-S}	210					
	δ_{NCS}	450				460	
	ν_{CN}	2162 2121				2110[e] 2075	
Ru(NH$_3$)$_5$NCS$^+$	ν_{Ag-S}	215					
	δ_{NCS}	465		460			
	ν_{CN}	2132	2130	2127	2124	2050[d] 2040	
Rh(NH$_3$)$_5$NCS^{2+}	ν_{CN}	2140				2115[d] 2070	

[a] ν_{Ag-S} = silver-sulfur stretch; δ_{NCS} = N-C-S bend; ν_{CS} = C-S stretch; ν_{CN} = C-N stretch.

[b] SERS band frequencies obtained for ca 1-5 mM complex in 0.01-0.1 M KCl + 3 mM HClO$_4$ at silver-aqueous interface at electrode potential indicated. Values listed are peak frequencies; for relative intensities, bandshapes see text and Figure 2. Obtained using 647.1 nm excitation; slightly different values of ν_{CN} obtained using 514.5 nm radiation (see text).
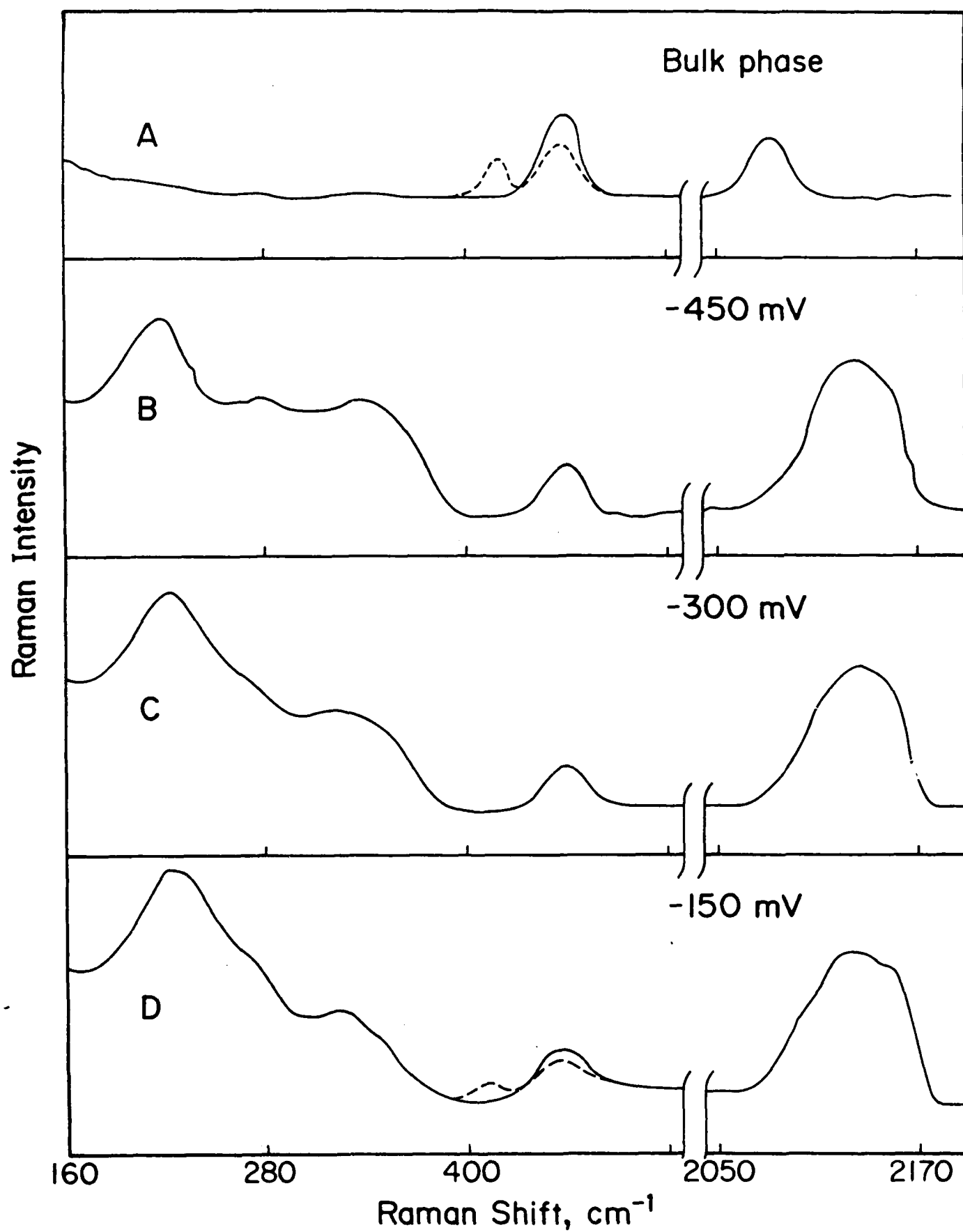
[c] Normal Raman and/or infrared peak frequencies obtained for bulk solid complex. Raman data given except where indicated.
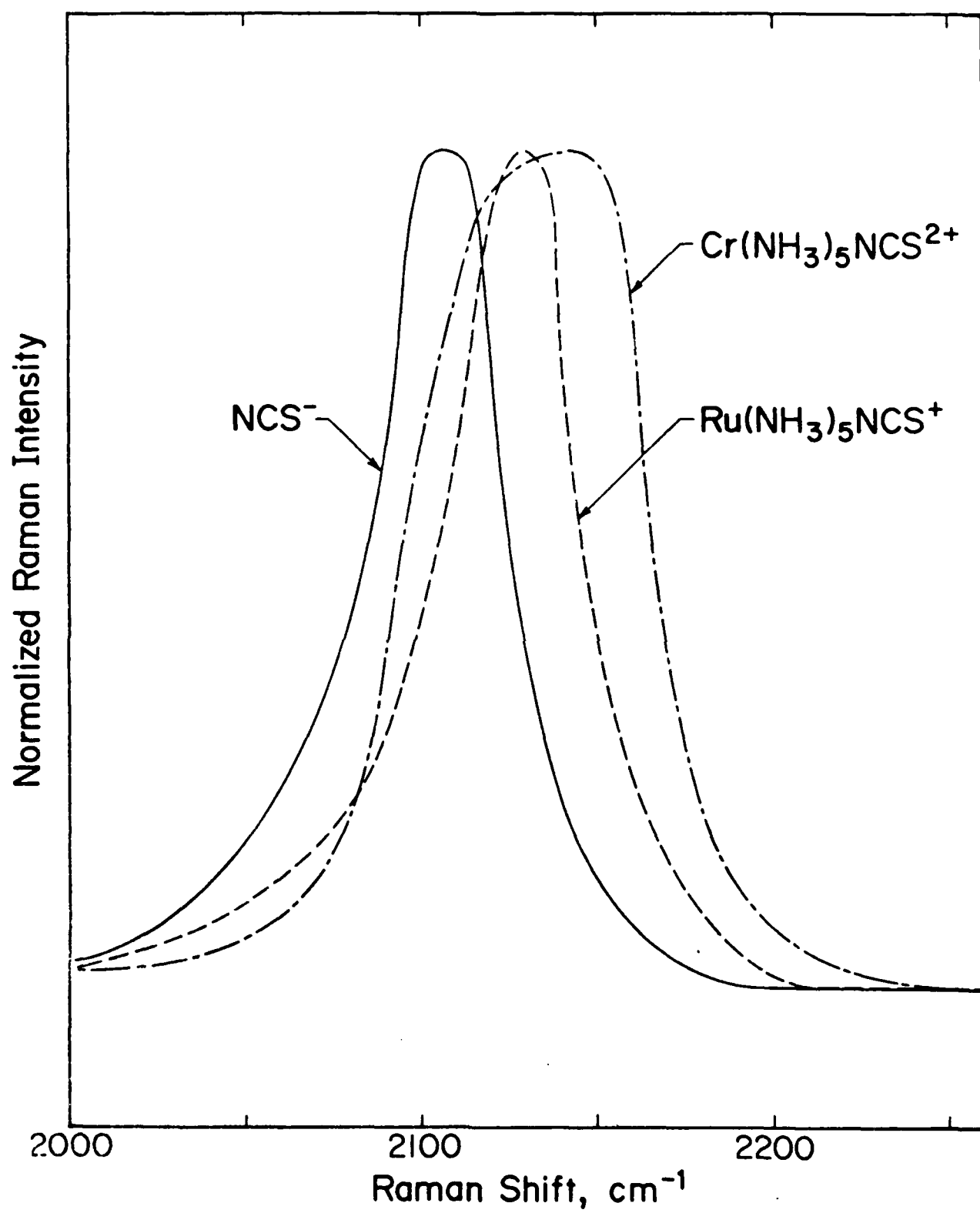
[d] Infrared data.
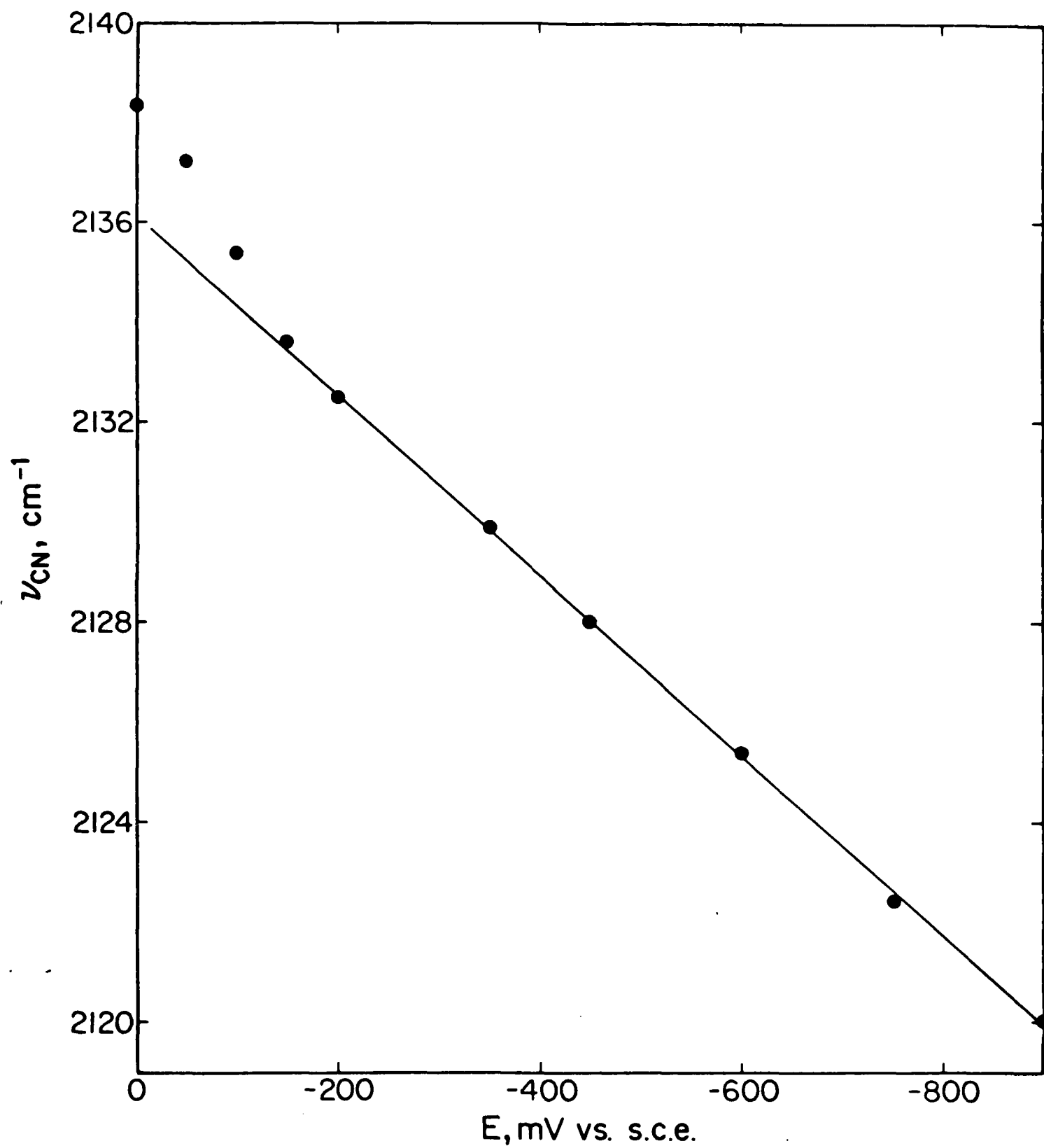
[e] Both Raman and Infared data.

[f] Infrared peak frequencies obtained for solid binuclear complex with S coordinated to Ag(I).

[g] Tentative assignment - IR band is broad and ill defined.

Bulk phase

A

−450 mV

B

−300 mV

C

−150 mV

D

Raman Intensity

160   280   400   2050   2170

Raman Shift, cm⁻¹

Figure Captions
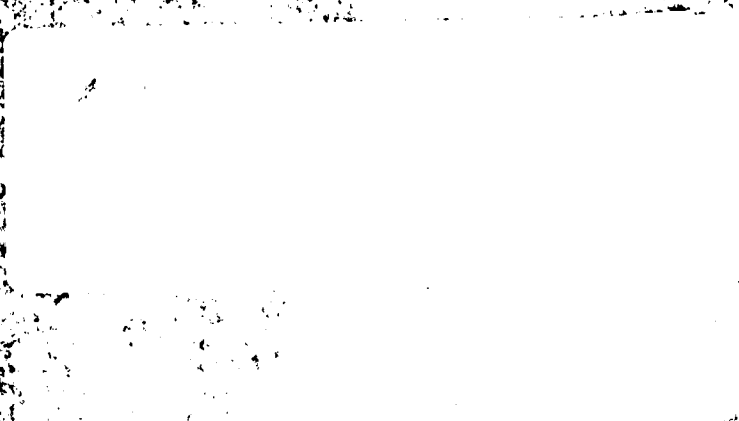
Figure 1.   Bulk-phase (A) and surface-enhanced Raman spectra (B-D) at silver electrode for $c\text{-}Cr(NH_3)_4(NCS)_2^+$ obtained using scanning Raman spectrometer with 647.1 nm laser excitation. Dashed lines refer to spectral segments determined for deuterated complex. SER spectra are for 1 $\underline{mM}$ complex in 0.01 $\underline{M}$ KCl + 2 $\underline{mM}$ HClO$_4$. For other conditions, see text.

Figure 2.   Surface-enhanced Raman C-N stretch bands for adsorbed NCS^-, $Cr(NH_3)_5NCS^{2+}$, and $Ru(NH_3)_5NCS^+$ at silver at -300 mV vs s.c.e., obtained using 647.1 nm laser excitation. Peak intensities are normalized to a common value; however, actual intensities were within ca twofold of each other.

Figure 3.   Peak frequency of SER ν_{CN} band for adsorbed $Ru^{II}(NH_3)_5NCS^+$ as a function of electrode potential. Solution contained 1 $\underline{mM}$ $Ru^{III}(NH_3)_5NCS^{2+}$ in 0.1 $\underline{M}$ KCl; 647.1 nm laser excitation. Slope of straight line is 18.0 cm^{-1} V^{-1}.

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